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(54) FUNGICIDAL COMPOSITIONS

(71) We, NIPPON KAYAKU KABUSHIKI KAISHA, of 6, Marunouchi 1-chome, Chiyoda-ku, Tokyo, a Company organised under the Laws of Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fungicidal compositions for agricultural and horticultural use.

According to the present invention there is provided a fungicidal composition for agricultural or horticultural use, which comprises, as active ingredients, a mixture of 1 part by weight of at least one metal complex of 8-hydroxyquinoline and from 0.1 to 10 parts by weight of at least one metal salt of α - amino - γ - ethylthiobutyric acid. The present invention also provides a method of combating fungus diseases in plants wherein the plants are treated with the composition just indicated.

Among the active ingredients, just indicated, cupric 8-quinolinolate which is a typical metal complex of 8-hydroxyquinoline, has already been proposed for use as a fungicide and has almost no phytotoxicity against plants. Furthermore, it has almost no side effects against human beings and cattle, but, when compared with other fungicides, has the disadvantage that its fungicidal effect is inferior to other fungicides.

On the other hand, the other active ingredient, i.e., the metal salt of α-amino-γ-ethylthiobutyric acid (hereinafter α-amino-γ-ethylthiobutyric acid is referred to as ethionine) has the disadvantage that its fungicidal effect is also inferior to other fungicides.

From researches which we have carried out with a view to removing the disadvantage i.e., the poor fungicidal effect of a metal complex of 8-hydroxyquinoline, it has been found that the present mixture possesses outstanding fungicidal activity at low concentrations due, apparently, to a synergistic effect whereby the fungicidal activity of the mixture is greater than that of each compound used separately.

The fungicidal composition of the present invention can be generally used for the control of pathogenic fungi, but it has a pronounced effect against *Alternaria kikuchiana* (Black spot of pear) and *Cochliobolus miyabeanus* (Helminthosporium leaf spot of rice plant) and is not poisonous to human beings, cattle or plants.

Examples of the metal complexes of 8-hydroxyquinoline which can be used in the present composition include the following compounds which can be used singly or as mixtures of two or more thereof:—

Name of compound	Melting point
1) cupric 8-quinolinolate	above 270°C
2) manganese 8-quinolinolate	"
3) zinc 8-quinolinolate	"
4) cobalt 8-quinolinolate	"
5) nickel 8-quinolinolate	"
6) iron 8-quinolinolate	"
7) lead 8-quinolinolate	"

[*Price 5s. 0d. (25p)*]

The following are examples of suitable metal salts of ethionine; again these salts may be used singly or as mixtures of two or more thereof:—

Name of compound	Melting point
1) copper ethionine	decomposed above 270°C.
2) manganese ethionine	"
3) zinc ethionine	"
4) cobalt ethionine	"
5) nickel ethionine	"
6) iron ethionine	"
7) lead ethionine	"

For a better understanding of the present invention, the fungicidal effect of the present mixture is illustrated by the following experiments.

EXPERIMENT I:

Spore germination test.

The spores of *Alternaria kikuchiana* (Black spot of pear) were mixed in Hopkins medium (pH 5) containing a predetermined concentration of the fungicidal composition indicated in Table 1 below, and the spore germinating ratio was observed after 18 hours incubation; the result is given in Table 1.

TABLE I

Names of compounds and concentrations of active ingredients (mcg/ml)		Spore germinating ratio (%)
Cupric 8-quinolinolate	Copper ethionine	
2.5	0	80.8
1.5	1.0	20.5
1.25	1.25	22.7
1.0	1.5	50.3
0	2.5	86.6
Zinc 8-quinolinolate	Zinc ethionine	
25	0	70.4
15	10	65.9
12.5	12.5	0
10	15	64.8
0	25	94.9

TABLE I (Continued)

Names of compounds and concentrations of active ingredients (mcg/ml)		Spore germinating ratio (%)
Manganese 8-quinolinolate	Manganese ethionine	
25	0	80.5
15	10	30.3
12.5	12.5	30.0
10	15	50.4
0	25	96.5
Lead 8-quinolinolate	Lead ethionine	
50	0	70.0
30	20	30.0
25	25	28.5
20	30	60.0
0	50	90.5
Cobalt 8-quinolinolate	Cobalt ethionine	
50	0	77.3
30	20	31.2
25	25	30.8
20	30	78.5
0	50	93.6
Nickel 8-quinolinolate	Nickel ethionine	
50	0	89.8
30	20	31.6
25	25	33.2
20	30	76.5
0	50	91.8

TABLE I (Continued)

Names of compounds and concentrations of active ingredients (mcg/ml)		Spore germinating ratio (%)
Iron 8-quinolinolate	Iron ethionine	
50	0	96.5
30	20	43.5
25	25	31.5
20	30	78.9
0	50	96.7
Cupric 8-quinolinolate	Zinc ethionine	
25	0	60.0
15	10	20.0
12.5	12.5	10.0
10	15	31.2
0	25	59.5
Zinc 8-quinolinolate	Manganese ethionine	
25	0	70.4
15	10	63.0
12.5	12.5	21.5
10	15	74.0
0	25	96.5
Manganese 8-quinolinolate	Lead ethionine	
25	0	80.5
15	10	65.2
12.5	12.5	38.0
10	15	75.5
0	25	90.5
Lead 8-quinolinolate	Cobalt ethionine	
50	0	70.0
25	25	34.0
20	30	65.0
0	50	93.6

TABLE I (Continued)

Names of compounds and concentrations of active ingredients (mcg/ml)		Spore germinating ratio (%)
Cobalt 8-quinolinolate	Nickel ethionine	
50	0	77.3
25	25	43.5
20	30	55.2
0	50	91.8
Nickel 8-quinolinolate	Iron ethionine	
50	0	89.8
25	25	45.0
20	30	65.0
0	50	96.7
Zinc 8-quinolinolate	Copper ethionine	
5.0	0	99.3
2.5	2.5	43.0
0	5.0	78.8
Manganese 8-quinolinolate	Copper ethionine	
5.0	0	96.8
2.5	2.5	51.3
0	5.0	78.8
Lead 8-quinolinolate	Copper ethionine	
5.0	0	97.8
2.5	2.5	53.5
0	5.0	78.8
Cobalt 8-quinolinolate	Copper ethionine	
5.0	0	98.2
2.5	2.5	61.0
0	5.0	78.8

TABLE I (Continued)

Names of compounds and concentrations of active ingredients (mcg/ml)		Spore germinating ratio (%)
Nickel 8-quinolinolate	Copper ethionine	
5.0	0	97.6
2.5	2.5	60.2
0	5.0	78.8
Iron 8-quinolinolate	Copper ethionine	
5.0	0	96.8
2.5	2.5	60.4
0	5.0	78.8

As is apparent from Table 1, the mixture of the present invention, i.e., a metal complex of 8-hydroxyquinoline and a metal salt of ethionine showed a pronounced inhibition of the spore-germination of *Alternaria Kikuchiana* when compared with the cases in which each component was used respectively.

EXPERIMENT 2:

The preventive effect on the disease of black spot of pear (*Alternaria Kikuchiana*) by means of the detached leaf test.

A detached leaf of pear (Niju Seiki species) was dipped into an aqueous solution containing a predetermined concentration of a fungicidal composition, and it was taken out and dried. Thereafter spores of *Alternaria Kikuchiana* were inoculated on the leaf by means of spraying, and the inoculated leaf was kept in a moist chamber at 27°C. The degree of disease development was observed.

The results obtained are shown in Table 2 and Table 3.

The degree of the development of disease was classified into the following six grades.

		Index of disease development
Healthy		0
Diseased area	1— 20%	1
	21— 40%	2
	41— 60%	3
	61— 80%	4
	81—100%	5

TABLE 2

Names of compounds and concentrations of active ingredients (mcg/ml)		Index of disease development
Cupric 8-quinolinolate	Copper ethionine	
250	0	4.5
150	0	5.0
125	0	5.0
100	0	5.0
0	250	3.0
0	150	4.0
0	125	5.0
0	100	5.0
150	100	1.5
125	125	0.5
100	150	0.5
Manganese 8-quinolinolate	Manganese ethionine	
250	0	3.0
150	0	4.8
125	0	4.5
100	0	5.0
0	250	4.0
0	150	5.0
0	125	5.0
0	100	5.0
150	100	1.5
125	125	2.0
100	150	3.5

TABLE 2 (Continued)

Names of compounds and concentrations of active ingredients (mcg/ml)		Index of disease development
Zinc 8-quinolinolate	Zinc ethionine	
300	0	3.0
200	0	4.5
0	200	5.0
0	250	5.0
0	300	5.0
0	500	4.0
300	200	0.5
250	250	1.0
200	300	1.5
Lead 8-quinolinolate	Lead ethionine	
500	0	3.5
300	0	4.5
250	0	5.0
200	0	5.0
0	500	4.0
0	300	4.5
0	250	5.0
0	200	5.0
300	200	1.5
250	250	2.0
200	300	2.0

TABLE 2 (Continued)

Names of compounds and concentrations of active ingredients (mcg/ml)		Index of disease development
Cobalt 8-quinolinolate	Cobalt ethionine	
500	0	4.0
300	0	5.0
250	0	5.0
200	0	5.0
0	500	5.0
0	300	5.0
0	250	5.0
0	200	5.0
300	200	2.5
250	250	2.0
200	300	2.5
Nickel 8-quinolinolate	Nickel ethionine	
1000	0	4.0
500	0	4.5
250	0	5.0
0	1000	4.5
0	500	5.0
0	250	5.0
500	250	2.5
250	250	2.5

TABLE 2 (Continued)

Names of compounds and concentrations of active ingredients (mcg/ml)		Index of disease development
Iron 8-quinolinolate	Iron ethionine	
1000	0	4.5
500	0	5.0
250	0	5.0
0	1000	4.0
0	500	5.0
0	250	5.0
500	500	2.5
250	250	2.0
"Difolatan"*		
250		2.5

*Registered Trade Mark for N-tetrachloroethylthio-tetrahydrophthalimide.

TABLE 3

Names of compounds and concentrations of active ingredients (mcg/ml)			Index of disease development
Manganese 8-quinolinolate	Cobalt ethionine	Copper ethionine	
250	0	0	4.5
150	0	0	5.0
125	0	0	5.0
100	0	0	5.0
0	250	0	4.0
0	150	0	5.0
0	125	0	5.0
0	100	0	5.0
0	0	250	3.0
0	0	150	4.0
0	0	125	5.0
0	0	100	5.0
100	100	50	1.5
50	50	150	0.5
25	25	200	1.0

EXPERIMENT 3:

The preventive effect on the disease of Helminthosporium leaf spot of rice plant (*Cochliobolus miyabeanus*)

10 ml. per pot of an aqueous solution containing a predetermined concentration of a fungicidal composition was sprayed on 20 seedlings of rice plants in a pot at the stage when three leaves had developed, and after the solution had dried, the seedlings were inoculated with a spore suspension of *Cochliobolus miyabeanus* and kept in a moist chamber overnight and thereafter kept in greenhouse. Five days after inoculation, the number of spots were counted.

The results obtained are shown in Tables 4 and 5.

The preventive value in the table was calculated in accordance with the following equation:

$$\text{Preventive value } (\%) = \left(1 - \frac{\text{number of spots per one leaf of treated plot}}{\text{number of spots per leaf of untreated plot}}\right) \times 100$$

TABLE 4

Names of compounds and concentrations of active ingredients (ppm.)		Preventive value (%)
Cupric 8-quinolinolate	Copper ethionine	
200	0	40.5
150	50	87.9
100	100	92.8
50	150	81.7
0	200	43.2
Zinc 8-quinolinolate	Zinc ethionine	
500	0	48.2
250	250	89.4
0	500	55.3
Manganese 8-quinolinolate	Manganese ethionine	
500	0	63.4
250	250	88.2
0	500	64.3
Lead 8-quinolinolate	Lead ethionine	
500	0	62.1
250	250	70.0
0	500	32.7
Cobalt 8-quinolinolate	Cobalt ethionine	
500	0	41.8
250	250	48.6
0	500	35.5
Nickel 8-quinolinolate	Nickel ethionine	
500	0	42.2
250	250	50.9
0	500	30.4

TABLE 4 (Continued)

Names of compounds and concentrations of active ingredients (ppm.)		Preventive value (%)
Iron 8-quinolinolate	Iron ethionine	
500	0	45.5
250	250	60.2
0	500	23.9

TABLE 5

Names of compounds and concentrations of active ingredients (ppm.)			Preventive value (%)
Cupric 8-quinolinolate	Zinc ethionine	Copper ethionine	
200	0	0	40.5
182	10	8	79.8
175	12	13	80.1
100	50	50	86.5
75	50	75	98.0
25	50	125	87.4
18	82	100	85.1
0	200	0	20.5
0	0	200	43.2

As is apparent from Tables 4 and 5, the mixture of the present invention can effectively prevent Helminthosporium leaf spot of rice plant (*Cochliobolus miyabeanus*).

On the other hand, no phytotoxicity against rice plants was observed.

In the mixture of the present invention, the most appropriate blending ratio can be determined in accordance with the growing condition and stage of the particular plant or plants to be treated, and the blending ratio is 1 part by weight of one or more kinds of metal complex of 8-hydroxyquinoline to 0.1 to 10 parts by weight of one or more kinds of metal salt of α-amino-γ-ethylthio butyric acid.

When the mixture of the present invention is used, it can be used in the form of a dry powder, a wettable powder, tablets or granules which can be applied directly alone or in admixture with a diluent or carrier.

Examples of carriers which may be used in the present compositions include, clay, talc, diatomaceous earth, bentonite and like solid carriers.

On the other hand, it is also possible to enhance the effect by mixing the composition with a dispersing agent, an emulsifier or a wetting agent so that it can be presented in a form suitable for application by spraying. The composition can also be mixed with a binding agent.

The present composition can also be mixed with a fungicide, insecticide, nematocide, herbicide, plant growth regulator, soil conditioner, fertilizer or other adjuvant conventionally used for agricultural or horticultural purposes.

This invention will now be further explained by the following non-limiting Examples in which all parts are parts by weight:—

EXAMPLE 1:

3 parts of manganese 8-quinolinolate, 2 parts of manganese ethionine, and 95 parts

of clay or talc were mixed and crushed to prepare a powder which was capable of being directly sprayed.

EXAMPLE 2:

12 parts of cupric 8-quinolinolate, 8 parts of copper ethionine, 77 parts of clay, and 3 parts of sodium long chain fatty alcohol sulphonate as a wetting agent were crushed and mixed to prepare a wettable powder which could be readily dispersed and suspended in water for fungicidal use.

WHAT WE CLAIM IS:—

1. A fungicidal composition for agricultural or horticultural use, which comprises, as active ingredients, a mixture of 1 part by weight of at least one metal complex of 8-hydroxyquinoline and from 0.1 to 10 parts by weight of at least one metal salt of α-amino-γ-ethylthiobutyric acid.

2. A fungicidal composition as claimed in Claim 1, wherein the metal complex of 8 - hydroxyquinoline is cupric, manganese, zinc, cobalt, nickel, iron or lead 8-quinolinolate or a mixture of two or more thereof.

3. A fungicidal composition as claimed in Claim 1 or 2, wherein the metal salt of α - amino - γ - ethylthiobutyric acid is the copper, manganese, zinc, cobalt, nickel, iron or lead salt, or a mixture of two or more thereof.

4. A fungicidal composition as claimed in any preceding claim, wherein the metal complex of 8 - hydroxyquinoline is cupric 8 - quinolinolate and the metal salt of α - amino-γ-ethylthiobutyric acid is copper α-amino-γ-butylthiobutyrate.

5. A fungicidal composition as claimed in any one of Claims 1 to 3, wherein the metal complex of 8 - hydroxyquinoline is zinc 8 - quinolinolate and the metal salt of α - amino - γ - ethylthiobutyric acid is zinc α - amino - γ - ethylthiobutyrate.

6. A fungicidal composition as claimed in any one of Claims 1 to 3, wherein the metal complex of 8 - hydroxyquinoline is manganese 8 - quinolinolate and the metal salt of α - amino - γ - ethylthiobutyric acid is manganese α-amino-γ-ethylthio-butyrate.

7. A fungicidal composition as claimed in any preceding claim, wherein the composition also comprises one or more adjuvants such as a dispersing agent, emulsifier, wetting agent or binding agent.

8. A fungicidal composition for agricultural and horticultural use in accordance with Claim 1 substantially as hereinbefore described in any one of the foregoing Experiments and Examples.

9. A method of combating fungus diseases in plants wherein the plants are treated with a composition as claimed in any one of Claims 1 to 8.

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